

UDC 666.295:546.82

SPECIFICS OF PHASE SEPARATION IN ZIRCONIUM-BEARING GLAZED GLASSES

I. A. Levitskii¹

Translated from Steklo i Keramika, No. 3, pp. 19–22, March, 2003.

The results of studying phase separation in zirconium-bearing alumoboron silicate glazed glasses at the stages of melting and thermal treatment are described. The effect of glass composition on the specifics of its phase composition and structure is considered. The possibility of producing low-melting glaze coatings with preset properties is demonstrated.

The topicality of development of zirconium-bearing glazed glasses is due to the need for improving the whiteness and covering power of coatings to camouflage insufficiently decorative color or non-uniform color tone in majolica products, which is caused by the universal use of local iron-bearing clays in majolica mixtures.

In developing lustrous opacified glazes we selected high-calcium alumoboron-bearing glasses with a low zirconium oxide content, i.e., 4% (here and elsewhere molar content is indicated) and a content of boron oxide not more than 15%. The purpose of the present study is to identify the phase-separation processes, namely, liquation and crystallization typical of the specified system, in order to synthesize opacified glazes with a prescribed set of properties. To achieve this purpose, glasses were synthesized within the system $\text{Na}_2\text{O} - \text{CaO} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$ with a substantial quantity of CaO that stimulates metastable liquation in glasses. The content of the main oxides varied within the following limits (%): 6.0–13.5 Na_2O , 5.0–17.5 B_2O_3 , and 5.0–15.0 Al_2O_3 .

The obtained glasses can be divided into three types: clear, opacified, and partly opacified in the form of flaky inclusions or white smears. Opacification in glasses is due to limited solubility of zirconium-bearing components in a silicate melt and formation of crystals of zirconium compound in cooling; therefore, the boundaries of clear glasses are simultaneously isotherms of ZrO_2 solubility in the melt. The effect of various oxides on glass formation and opacification of zirconium glasses is related to the solubility of zirconium compounds.

Thus, the positive effect of Na_2O and CaO is due to the fact that the number of modifier ions grows with increasing basicity of the glass, and favorable conditions are created for transition of Zr^{4+} from the cation part of the structure to the mixed anion skeleton in the form of six-coordination groups

$[\text{ZrO}_6]^{2-}$. In this case, the solubility of ZrO_2 improves in proportion to the content of oxides of alkali and alkali-earth metals. The opacifying effect in this case decreases. Aluminum oxide also has a perceptible effect on the solubility of ZrO_2 . As the content of Al_2O_3 increases above 10.0%, the range of opacified glasses expands. Aluminum ions in experimental glasses presumably exist in a four-coordination state due to the formation of complex groups $[\text{AlO}_{4/2}]^{\text{Na}}$ and $[\text{AlO}_{4/2}]^{\text{Ca}_{0.5}}$. As the content of Al_2O_3 increases, the majority of modifier ions is going to be bonded in these groups. In such a case, the excessive quantity of ZrO_2 remaining in the cation part of the structure, which determines opacification, increases. B_2O_3 has a less perceptible effect on the opacification process.

An increased content of Na_2O , as could be expected, significantly decreases the viscosity of glasses, whereas an increase in the content of Al_2O_3 above 10.0% significantly increases it.

The study of glasses by the DTA method indicates that all sections typically exhibiting endothermic effects in the temperature range of 610–700°C split into two, which is due to a modification in the heat capacity of the glass in softening and also due to the liquid-type phase separation, i.e., liquation. Thermograms also exhibit exothermic effects in a temperature interval of 930–1000°C, whose intensity is determined by the content of CaO and the ratio of $\text{Al}_2\text{O}_3 : \text{B}_2\text{O}_3$ in the glass composition.

A sharp increase in the DTA curves points to a higher crystallization capacity of glasses with an increased content of CaO . With a minimum content of CaO (which is 7.5%), crystallization phenomena are observed with a content of B_2O_3 equal to 12.5–15.0% and with minimal quantities of Al_2O_3 (5.0–7.5%). As the content of CaO increases to 15.0%, the maximum degree of crystallization is registered in samples containing 7.5 and 10.0% B_2O_3 and 10.0–12.5% Al_2O_3 .

¹ Belarus State Technological University, Minsk, Belarus.

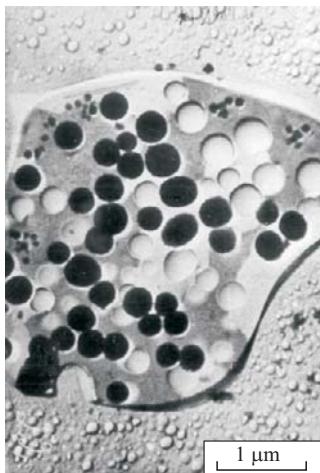


Fig. 1. Electron microscope photo of glass of composition $10.5\text{Na}_2\text{O} \cdot 10.5\text{CaO} \cdot 15\text{Al}_2\text{O} \cdot 7.5\text{B}_2\text{O}_3 \cdot 52.5\text{SiO}_2 \cdot 4\text{ZrO}_2$ investigated by x-ray spectral microprobe analysis.

Electron microscope studies of glasses point to the liquation type of phase separation in visually clear, as well in opalescent and opacified glasses. The liquation origin of inhomogeneities is evidenced by their x-ray amorphousness. It is established that CaO has the most significant effect on opacification of zirconium-free glasses. In an equimolar substitution of CaO for Na_2O , the quantity of drops per volume unit significantly grows and the nature of liquation separation changes. Thus, with a CaO content equal to 7.5%, liquation separation of a transitional type is observed: both drop and two-skeleton formations are registered. The sizes of the two-skeleton heterogeneities are 0.4–1.0 μm ; those of drop heterogeneities are 0.1–0.3 μm . When Na_2O is replaced by CaO in an amount up to 10.0%, liquation acquires the drop form, drops sized around 0.2 μm are uniformly distributed in the glass matrix, and their quantity per volume unit significantly grows. An increase in the content of CaO up to 15.0% decreases nearly by half the drop size and their number per volume unit is nearly doubled. As for a correlation between the type of liquation and the quantity of B_2O_3 , the diameter of heterogeneities grows insignificantly with increasing content of B_2O_3 and drop liquation prevails.

Al_2O_3 actively suppresses liquation processes in glasses of the considered system. Glasses with a low content of Al_2O_3 typically have the transitional type of liquation. As the content of Al_2O_3 increases, heterogeneities sized over 1 μm decrease and become isolated as single drops; with a content of Al_2O_3 equal to 10%, the drop size is 0.1–0.3 μm . The quantity of heterogeneities per volume unit also decreases with increasing content of Al_2O_3 , which indicates a rearrangement of the glass structure.

Local x-ray spectral analysis was performed to identify the elemental composition of phases in liquating glasses. A drop was grown in solid glass (Fig. 1) for 36 h at a temperature of 750–780°C. As a consequence of protracted heat treatment, drops sized over 3 μm were grown. Based on the x-ray spectral analysis data, it can be inferred that the glass matrix is formed by highly polymerized aluminosilicate components including Na_2O , as Na^+ is essentially totally lo-

calized on tetrahedrons $[\text{AlO}_4]$. The drop phase is represented by a low-silica calcium-borate component that contains zirconium as well.

The effect of heat treatment on the structure of opacified and clear initial glasses was studied using the forced crystallization method within a temperature range of 650–1000°C in a gradient furnace and also by protracted heat treatment under selected temperature conditions. Glasses with a low content of Al_2O_3 are not prone to crystallization. The total absence of ZrO_2 in the crystalline phase at the first stages of heat treatment is presumably a consequence of the incorporation of zirconium ions into the common anion skeleton in the form of six-coordinated groups $[\text{ZrO}_6]^{2-}\text{Na}^+$ and $[\text{ZrO}_6]^{2-}\text{Ca}^{2+}$. Participation of modifier ions in the formation of electroneutral complex groups is responsible for the high degree of cohesion of the silicon-oxygen skeleton.

As the content of Al_2O_3 and CaO grows, the propensity of glasses for crystallization grows as well. The products of crystallization contain ruffite, which is a tetragonal modification of ZrO_2 , ZrSiO_4 , and in some compositions sodium orthosilicate. The tendency of experimental glasses to crystallization with an increasing content of Al_2O_3 is also due to the structural specifics of zirconium-bearing aluminoborosilicate glasses. A shortage of weakly fixed oxygen carried by modifier ions limits the number of Zr^{4+} that may be incorporated in the common anion skeleton in the form of groups $[\text{ZrO}_6]^{2-}\text{R}_2^+$ and $[\text{ZrO}_6]^{2-}\text{R}^{2+}$. In this case, an excessive amount of Zr^{4+} remains in the cation part of the structure in the form of $[\text{ZrO}_8]$ groups. Incorporation of large zirconium groups into the cation part of glass loosens its structure and facilitates the crystallization of zirconium compounds in the course of heat treatment.

Electron microscope study of glasses of all types (clear, partly or completely opacified, and glasses with a surface film) indicated that they have a liquation structure, which is even more perceptible under thermal treatment within a temperature interval of 650–900°C. Thus, in heat treatment at 700°C for 2 h a more evident liquation structure is revealed in visually transparent glasses. Liquation heterogeneities in initial glasses are of a two-skeleton type. Their size is 0.2–0.4 μm . Transition to drop liquation is registered in heat treatment, which is more perceptible as temperature increases from 700 to 850°C. The prevailing drop size is 0.03–0.10 μm . The formation of crystalline phases is registered under heat treatment within a temperature interval of 900–1000°C, including ruffite ZrO_2 , zircon ZrSiO_4 , and sodium orthosilicate Na_2SiO_4 . The shape of the new formations is close to cross-shaped doublets and stars and is typical of ruffite. A further increase in temperature changes the habitus and size of the crystals: they acquire a prismatic shape and sizes up to 0.5–1.0 μm .

The process of growth of crystalline formations is registered already at 850°C, when new formations, whose habitus remotely resembles a prismatic one, originate on liquation heterogeneities. The sizes of crystalline heterogeneities are

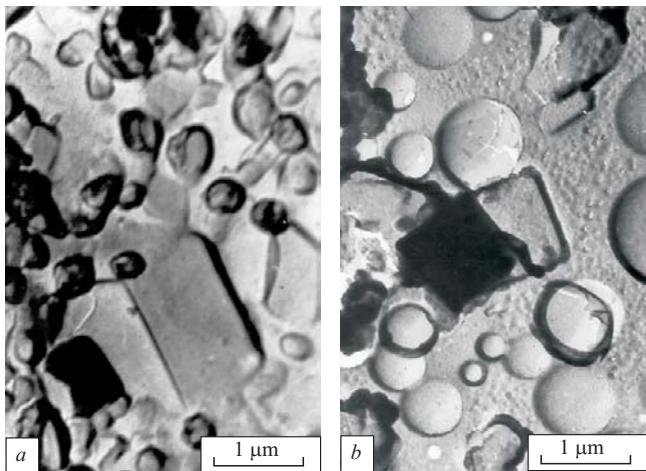


Fig. 2. Electron microscope photos of products of heat-treatment of glasses of compositions $13.5\text{Na}_2\text{O} \cdot 7.5\text{CaO} \cdot 7.5\text{B}_2\text{O}_3 \cdot 12.5\text{Al}_2\text{O}_3 \cdot 55\text{SiO}_2 \cdot 4\text{ZrO}_2$ (a) and $10.5\text{Na}_2\text{O} \cdot 10.5\text{CaO} \cdot 15\text{B}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3 \cdot 55\text{SiO}_2 \cdot 4\text{ZrO}_2$ (b).

0.2 – 0.4 μm . Liquation in samples heat-treated at a temperature of 900°C and higher is not registered.

Such phase transitions are registered as well in liquating glasses that become partly opacified in melting. Initial glasses have liquation heterogeneities of the two-skeleton type; under heat treatment they transform into drop liquation with a size of heterogeneities up to 0.2 – 0.3 μm . The drops act as centers of nucleation of crystalline heterogeneities (Fig. 2). As the temperature of heat treatment increases, the crystals acquire a better defined prismatic shape, their length ranges from 0.2 to 1.0 μm , and clusters are formed at a temperatures of 1050°C. The main crystalline phases of the products of heat treatment of glasses at 950 – 1000°C are ruffite and zircon.

Glasses opacified in the course of melting retain their opacification within a temperature interval of 850 – 1100°C. At the same time, they exhibit slight dullness and intensified opacification due to surface film crystallization.

The type of crystalline formations in the products of glass crystallization depends on the chemical composition of the glass. Thus, with increasing quantity of Al_2O_3 the intensity of diffraction maximums of zirconium crystalline phases increases and that of sodium orthosilicate decreases (Fig. 3). One should note the positive effect of CaO increasing the quantity of zirconium formations, although there are reports on an adverse effect of CaO on opacification of zirconium-bearing glasses [1, 2].

A specific feature of the glasses considered is the immediate crystallization of a more symmetrical tetragonal form of ZrO_2 , which is presumably due to decreased surface energy at the crystalline seed – glass interface due to liquation segregation.

A study of the heat-treatment effect on the structure of liquating glasses under isothermal conditions at a temperature of 800°C for 4 – 6 h revealed typical secondary separa-

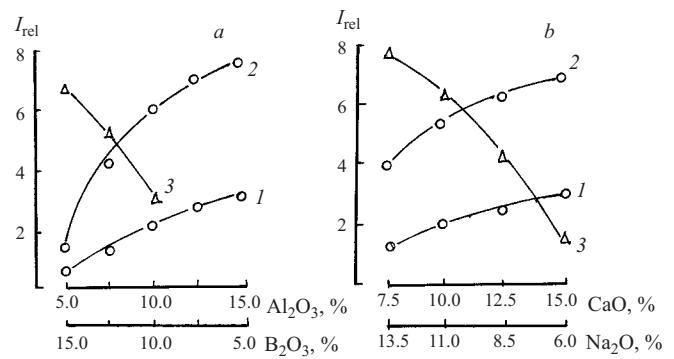


Fig. 3. Relative content of crystalline phases in products heat-treated at 950°C versus a content of Al_2O_3 (a) and CaO (b): 1) ruffite ($d = 0.294 \text{ nm}$); 2) zircon ($d = 0.303 \text{ nm}$); 3) sodium orthosilicate ($d = 0.681 \text{ nm}$).

tion, especially in samples with an increased CaO content (15.0%). The size of larger heterogeneities is 0.6 – 0.7 μm ; the size of secondary drops is not more than 0.05 – 0.10 μm .

The specifics of the kinetics and morphology of phase separation in glasses of the particular system were studied using the method in [3] employing statistical processing of electron microscope photos and calculation of quantitative characteristics of the liquation structure: the total number of particles per volume unit, the function of size distribution of particles, the ratio of volumes of coexisting phases and mean particle radii. The studies were carried out on samples obtained by melt cooling and heat-treated under isothermal conditions at a temperature of 700 – 900°C for 24 h.

It is established that liquation at the initial stages of thermal treatment is of the two-skeleton type. Transition to a binodal type of liquation occurs relatively slowly: a drop structure emerges at 650°C after an exposure for 18 h; an increase in temperature to 750°C leads to the formation of spherical drops in 2 – 3 h. Hence it follows that either the oxides introduced modify the mechanism of phase disintegration or differences in phase morphology reflect the specifics of the early and the later phases, there being a unique mechanism of disintegration. Relationships of the relative volume of the drop phase to the duration and temperature of heat treatment, the mean radius of particles, and the total number of particles per volume unit of glass of composition $10.5\text{Na}_2\text{O} \cdot 10.5\text{CaO} \cdot 15\text{B}_2\text{O}_3 \cdot 7.5\text{Al}_2\text{O}_3 \cdot 52.5\text{SiO}_2 \cdot 4\text{ZrO}_2$ are shown in Fig. 4. Analyzing the results of investigations, one can infer that an equilibrium state of vitreous phases in zirconium-bearing glasses is achieved relatively slowly and transition to a drop structure requires a longer heat treatment.

Thus, the mechanism of phase separation in glasses of the $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$ system depends on ZrO_2 . Its homogenizing effect is manifested in delaying the processes of formation of an equilibrium liquation drop structure.

Raman scattering spectroscopy offered certain conclusions with respect to the short-range order of their structure and coordination of elements. Raman scattering spectra of

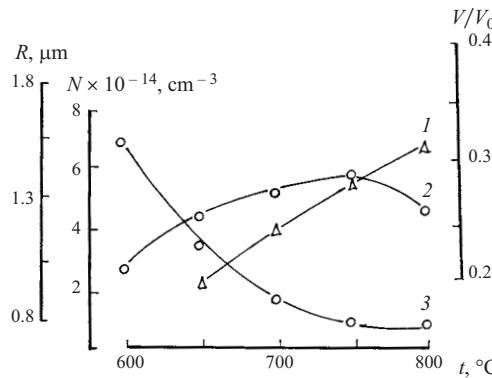


Fig. 4. Dependence of relative volume of the drop phase V/V_0 (1), mean particle radius R (2), and total number of particles per glass volume unit N (3) on the temperature t of heat treatment for 24 h.

initial glasses (Fig. 5) typically have three widened bands in a range of 800 and 1000 cm^{-1} . By comparing spectra known from the literature [4–7] and obtained experimentally, the following inferences can be made. The bands in the range of 460 and 1000 cm^{-1} correlate with Raman scattering which, according to the data in [8], is typical of groups $[\text{SiO}_4]$, and the band at 800 cm^{-1} is typical of trigonally coordinated boron [7]. A weak band in the range of 610–620 cm^{-1} is typical of tetrahedrally coordinated boron.

As the content of Al_2O_3 increases, the bands gradually become narrower and the nature of the spectra sharply changes. The emergence of narrow intense bands with maximums at 100, 180, 190, 335, 350, 395, 470, and 620 cm^{-1} indicates variations in the coordination number of Zr^{4+} from 6 to 8 and crystallization of ZrO_2 [4]. Consecutive introduction of Al_2O_3 leaves sufficient possibilities for zirconium ions to be incorporated in the anion structure of the glass; however, part of these ions in the form of $[\text{ZrO}_8]$ groups remains in the cation part and facilitates the formation of crystals. The crystalline phase was not identified in initial glasses using x-ray phase analysis due to its small quantity. The spectroscopic method makes it possible to clearly confirm the effect of Al_2O_3 on the solubility of zirconium compounds in the glasses considered. The spectra of glasses containing a maximum amount of Al_2O_3 (15.0%) show a decreased intensity of spectral bands, which may be evidence of a delay in the crystallization processes. This is presumably due to a sharp increase in the viscosity of the experimental glasses as the content of Al_2O_3 increases, which decreases the rate of formation of crystals and retards their growth.

A study of the glass structure using the Raman scattering spectroscopy method corroborated the presence of three- and four-coordinated boron. An increase in the content of aluminum oxide decreases the solubility limit of zirconium and facilitates its crystallization from the melt in the form of the crystalline modification ZrO_2 , namely, ruffite.

Glasses of the system $\text{Na}_2\text{O} - \text{CaO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{SiO}_2$ in the considered composition range have high physicochemical parameters: microhardness in the limits of

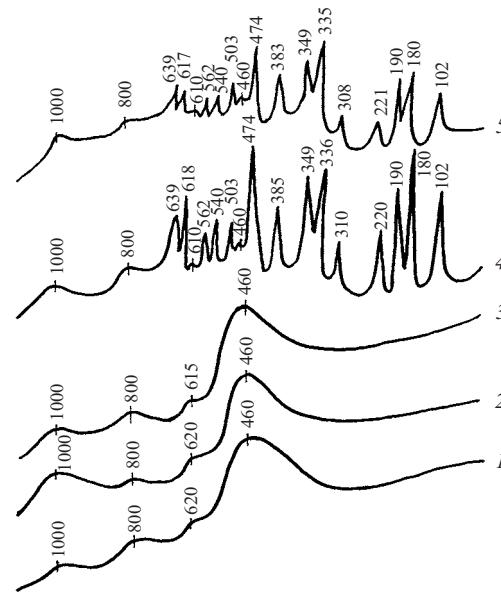


Fig. 5. Raman scattering spectra of glasses containing 10.5% Na_2O with a ratio of $\text{B}_2\text{O}_3 : \text{Al}_2\text{O}_3$ equal to 3.50 (1), 2.00 (2), 1.25 (3), 0.50 (4), and 0.20 (5).

5200–5850 MPa, density 2590–2640 kg/m^3 , chemical resistance (weight loss) 0.5–1.0% in H_2O , 5.27–8.26% in 1 N HCl, and 0.5–1.0% in 1 N NaOH. The TCLE of the specified composition provides for thermal expansion coordinated with ceramic substrate, which guarantees high quality of the glaze coating.

The results of firing of coatings in a temperature range of 700–1100°C indicate, based on glasses of the specified system, that it is possible to obtain glazes of different quality and texture, i.e., dull, lustrous, semidull, mainly opacified and with different fusion temperatures from 920 to 1000°C.

REFERENCES

1. H. Oel, H. Lechenmayr, and A. Dietzel, "Die zirkontrübung bei glasuren und emails," *Ber. Deutsch. Keram. Gesch.*, **42**(12), 462–467 (1965).
2. A. P. Petzold, *Enamel* [Russian translation], Metallurgizdat, Moscow (1958).
3. É. V. Morozova, A. M. Kalinina, and V. N. Filipovich, "Quantitative analysis of drop phase separation by example of sodium-borosilicate glass with and without ZrO_2 additive," *Fiz. Khim. Stekla*, **12**(4), 395–405 (1986).
4. C. M. Phillipi and K. S. Mazdiyasni, "Infrared and Raman spectra of zirconia polymorphs," *J. Am. Ceram. Soc.*, **54**(5), 254–258 (1971).
5. N. M. Bobkova, I. A. Levitskii, and S. A. Gailevich, "IR spectra of glasses with a decreased content of B_2O_3 ," *Zh. Prikl. Spektr.*, **63**(5), 870–872 (1996).
6. R. S. Tobias, I. A. Koningstein, O. S. Mortensen, et al., in: A. Anderson (ed.), *The Raman Effect, Vol. 2. Applications*, Marcel Dekker, New York (1973).
7. O. V. Yanush, V. O. Kabanov, and I. A. Mukhittdinova, "A study of sodium borate glasses using the Raman scattering spectroscopy method," *Fiz. Khim. Stekla*, **14**(3), 330–341 (1988).
8. W. L. Konijnendijk, "The structure of borosilicate glasses," *Phil. Rep. Suppl.*, No. 1, 243–246 (1975).